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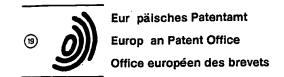
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# **EUROPEAN PATENT APPLICATION**

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Detergent composition.

© A fabric washing composition comprises a surfactant system including an 0-alkanoyl derivative of a reducing hexose sugar such as a 6-0-alkanoyl glucoside, together with a cosurfactant. The composition has advantages in terms of cost, biodegradability and performance.

#### **DETERGENT COMPOSITION**

This invention relates to a detergent composition, especially such a composition suitable for the washing of fabrics.

Fabric washing compositions traditionally contain one or more detergent active materials in addition to various other ingredients such as detergency builders, bleaches, fluorescers, perfumes etc. A number of different classes of detergent active materials have been proposed in the art, particular attention having recently been given to alkylpolyglycosides.

We have now found that a specific class of glucose derivatives have particular advantages in terms of cost and biodegradability, these can be described as glucose esters and belong to the class of O-alkanoyl derivatives of reducing hexose sugars.

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O-alkanoyl glucosides are described in International Patent Application WO 88/10147 (Novo Industri A/S). In particular the surfactants described therein are glucose esters with the acyl group attached in the 3or 6-position such as 3-O-acyl-D-glucose or 6-O-acyl-D-glucose. International Patent Application WO 89/01480 (Novo Industri A/S) describes glucose esters and their preparation using specific enzymes. Ethyl 6-O-alkanoyl glucosides are suggested for use as co-surfactants in a laundry detergent composition comprising linear alkyl benzene sulphonate and a phosphate builder.

European Patent Application EP 0 380 437 (Novo-Nordisk A/S and Procter and Gamble Co) describes the use of esters of monosaccharides in particular bleaching detergent compositions which optionally comprise linear alkylbenzene sulphonate as a co-surfactant.

We have now found that glucose esters when combined with certain co-surfacants give surprisingly good soil removal from textiles.

Thus, according to the invention there is provided a fabric washing composition comprising a surfactant system comprising an O-alkanoyl derivative of a reducing hexose sugar and a co-surfactant selected from the group of anionic detergent actives, nonionic detergent actives, zwitterionics detergent actives, amphoteric detergent actives, cationic detergent actives and semi-polar detergent actives except where the anionic detergent active is linear alkyl benzene sulphonate.

In the present invention we prefer to use a 6-O-alkanoyl glucoside, especially compounds having the formula (I):

R 
$$\sim$$
 C  $\sim$  O  $\sim$  35  $\sim$  OR  $^{1}$   $\sim$  OH  $\sim$  OH

wherein R is an alkyl or alkenyl group having from 7 to 18 carbon atoms, and R1 is hydrogen or an alkyl group having from 1 to 4 carbon atoms.

Most pr ferred are such compounds where R1 is an alkyl group, such as ethyl or isopropyl. Alkylation in the 1-position enables such compounds to be pr pared by regiospecific enzymatic synthesis as described

by Bjorkling et al. (J. Chem. Soc., Chem. Commum. 1989 p934) the disclose of which is incorporated herein by reference.

While the above description concerns surfactants based on glucose, it is envisaged that corresponding materials based on other reducing hexose sugars, such as galactose and mannose are also suitable.

The surfactant system consists of the alkanoyl glucose mixed with one or more cosurfactants. When R is at least C<sub>3</sub>, it is particularly preferred to use cosurfactants with a high HLB (such as above 10.5) and which exist in the micellar phase at concentrations in water up to at least 1 g/l. When R is less than C<sub>3</sub>, it is preferred to use a cosurfactant with an HLB below 10.5. The cosurfactants are selected from anionic or nonionic materials, although the possibility is not excluded of including zwitterionic, amphoteric, cationic or semi polar surfactants.

Preferably the co-surfactants will be present in a weight ratio of from 20:1 to 1:20, most preferably from 9:1 to 1:9 relative to the alkanoyl glucoside.

Examples of suitable anionic detergent surfactants are alkyl benzene sulphonates (excepting linear alkyl benzene sulphonates), alkyl ether sulphates, olefin sulphonates, alkyl sulphates, secondary alkyl sulphonates, fatty acid ester sulphonates, dialkyl sulphosuccinates, alkyl orthoxylene sulphonates and other disclosed in the literature, especially 'Surface Active Agents' Vol. I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the "McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981

Specific examples of alkyl benzene sulphonates include alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group.

Suitable alkyl and alkylether sulphates include those having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates have from 1 to 5 ethylene oxide groups.

Suitable olefin sulphonates are those prepared by sulphonation of  $C_{10}$ - $C_{24}$  alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product.

Specific examples of alkyl sulphates, or sulphated fatty alcohol salts, include those of mixed alkyl chain length, in which the ratio of C<sub>12</sub> alkyl chains to C<sub>18</sub> alkyl chains is in the range of from 9:4 to 1:6. A suitable material can be obtained from a mixture of synthetic lauryl and oleyl alcohols in appropriate properties.

Specific examples of fatty acid ester sulphonates include those of the general formula

wherein R1 is derived from tallow, palm or coconut oil and R2 is a short chain alkyl group such as butyl.

Specific examples of dialkyl sulphosuccinates include those in which both alkyl substituent contains at least 4 carbon atoms, and together contain 12 to 20 carbon atoms in total, such as di-C<sub>8</sub> alkyl sulphosuccinate.

Specific examples of alkyl orthoxylene sulphonates include those in which the alkyl group contains from 12 to 24 carbon atoms.

Other anionic surfactants which may be used include alkali metal soaps of a fatty acid, preferably one containing 12 to 18 carbon atoms. Typical of such acids are oleic acid, ricinoleic acid and fatty acids derived from caster oil, rapeseed oil, groundnut oil, coconut oil, palmkernal oil or mixtures thereof. The sodium or potassium soaps of these acids can be used. As well as fulfilling the role of surfactants, soaps can act as detergency builders or fabric conditioners.

Suitable nonionic surfactants which may be used are alkoxylated materials which are the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alon or with propyl ne oxid . Sp cific alkoxylat d nonionic d tergent compounds are alkyl ( $C_6$  -  $C_{22}$ ) phenols- thylene oxide condensates, the condensation products of aliphatic ( $C_8$  -  $C_{18}$ ) primary or s condary linear or branched alcohols with ethylene oxide, and products made by condensation of thyl ne oxide with the reaction products of propylene oxide and ethylenediamine.

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Alkylene oxide adducts of fatty materials are preferably used as the nonionic surfactants. The number of alkyl n oxide groups p r mol cule has a considerable eff ct upon the HLB of the nonionic surfactant. The chain length and nature of the fatty material is also influential, and thus the preferred number of alkylene oxide groups per molecule depends upon the nature and chain length of the fatty material.

Alkyl glycosides may be used as the nonionic surfactant for xample C<sub>9/1</sub> poly glycosides.

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The compositions of the invention will generally contain an electrolyte, preferably present in such an amount to give a concentration of at least 0.01 molar, most preferably at least 0.05 molar, most preferably at least 0.1 molar, when the composition is added to water at a concentration of 1 g/l, being approximately the lowest level at which detergent compositions are used in usual practice. More usual is usage at a level of 4 to 10 g/l and it is desirable to achieve an electrolyte concentration of 0.05M, most preferably at least 0.1M, when the composition is added to water at such levels. In particular, the presence of electrolyte is beneficial when an anionic cosurfactant is present. Where no anionic cosurfactant is used, beneficial results may be obtainable where no electrolyte is present, save perhaps that originating from the hardness of the water which may be as low as 6 x 10<sup>-4</sup> mol/l.

The level of electrolyte in the wash liquor is not, in practice, a parameter over which the domestic user of a fabric washing product has very much control. It is determined, inter alia by the level of water-soluble salts present in the product and the recommended dosage for that product. Thus forms of the present invention using alkyl groups with a total of 16 or more carbon atoms are of particular value in two circumstances, i.e. i) where recommended dosage levels are low, as for example in North America, and ii) where the product contains high levels of water-insoluble material, as for example where the product contains a water-insoluble detergency builder material.

The invention also embraces a method of washing fabrics by contact with a wash liquor containing, for example, from 0.5 g/l to 10 g/l of a composition as described herein.

Preferred compositions according to the invention include from 2% to 50%, such as from 4% or 6% to 30% by weight of the surfactant system.

It is desirable that the compositions according to the invention be approximately neutral or preferably alkaline, that is when the composition is dissolved in an amount to give surfactant concentration of 1 g/l in distilled water at 25°C the pH should desirably be at least 6, preferably at least 8 and yet more preferably at least 10. To this end the compositions may include a water-soluble alkaline salt. This salt may be a detergency builder (as described in more detail below) or a non-building alkaline material.

When the compositions of the invention contain a detergency builder material, this may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the compositions with other beneficial properties such as the generation of an alkaline pH and the suspension of soil removed from the fabric.

Examples of phosphorus-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous alumino silicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate (with or without calcite seeds, sodium and potassium bicarbonates and silicates.

Examples of organic detergency builders, when present include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxsulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present. Examples of other ingredients which may be present in the composition are polymers containing carboxylic or sulphonic acid groups in acid form or wholly or partially neutralised to sodium or potassium salts, the sodium salts being preferred. Preferred polymers are homopolymers and copolymers of acrylic acid and/or maleic acid or maleic anhydride. Of especial interest are polyacrylates, acrylic/maleic acid copolymers, and acrylic phosphinates.

The molecular weights of homopolymers and copolymers are generally 1000 to 150,000, preferably 1500 to 100,000. The amount of any polymer may lie in the range from 0.5 to 5% by weight of the composition. Other suitable polymeric materials are cellulose ethers such as carboxy methyl cellulos, methyl cellulose, hydroxy alkyl celluloses, and mixed ethers, such as methyl hydroxy ethyl cellulose, methyl hydroxy propyl cellulose, and methyl carboxy methyl cellulose. Mixtures of different cellulose ethers, such as methyl cellulose ethers, such as methyl hydroxy propyl cellulose, and methyl carboxy methyl cellulose. Mixtures of different cellulose ethers, such as methyl hydroxy propyl cellulose, and methyl carboxy methyl cellulose.

particularly mixtures of carboxy methyl cellulose and methyl cellulose, are suitable. Poly thylene glycol of molecular weight from 400 to 50,000, preferably from 1000 to 10,000, and copolymers of polyethylene oxide with polypropylene oxide are suitable as also are copolymers of polyacrylate with polyethylene glycol. Polyvinyl pyrrolidone of molecular weight of 10,000 to 60,000 preferably of 30,000 to 50,000 and copolymers of polyvinyl pyrrolidone with other poly pyrrolidones are suitable. Polyacrylic phosphates and related copolymers of molecular weight 1000 to 100,000, in particular 3000 to 30,000 are also suitable.

Further examples of other ingredients which may be present in the composition include fabric softening agents such as fatty amines, fabric softening clay materials, lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as cellulases, proteases, lipases and amylases, germicides and colourants.

The detergent compositions according to the invention may be in any suitable for including powders, bars, liquids and pastes. For example suitable liquid compositions may be non-aqueous or aqueous, the latter being either isotropic or lamellar structured. The compositions may be prepared by a number of different methods according to their physical form. In the case of granular products they may be prepared by dry-mixing, coagglomeration, spray-drying from an aqueous slurry or any combination of these methods. A preferred physical form is a granule incorporating a detergency builder salt. This may be prepared by conventional granulation techniques.

#### **EXAMPLES**

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In the following examples, alkyl alkanoyl glucosides of formula (I) were used in which R was as specified below and R¹ was ethyl.

Polyester fabric loaded with triolein was washed in various wash liquors and using standard techniques the percentage detergency was determined. The wash conditions were 20 minutes at 40°C. The wash liquors containing 1 g/l of the glucoside or its mixture with other detergent active materials as specified below and 0.05M sodium metaborate to maintain a pH of 10.7.

#### 35 Example 1

The results for the use of the glucoside as the only detergent active material were as follows:

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R	% Detergency
C <sub>9</sub>	74
C <sub>11</sub>	38
C <sub>13</sub>	30
C <sub>15</sub>	13
coconut alkyl	21

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These results show a preference for the C<sub>9</sub> substituted material.

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#### Example 2

When the R =  $C_{11}$  material was mixed in various proportions with  $C_{12}$  alkyl benzene sulphonate (LAS) the results were:

LAS/glucoside	% Detergency
ratio (wt)	
100/0	36
80/20	45
60/40	51
40/60	47
20/80	39
0/100	42

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These results show a benefit for a LAS/glucoside ratio between 4:1 and 2:3.

# Example 3

When the  $R = C_{11}$  material was mixed in various proportions with  $C_{12}$  alcohol ethoxylated with an average of 8 ethylene oxide groups per molecule (C12E8) the results were:

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C12E8/glucoside	% Detergency
ratio (wt)	
100/0	50
80/20	62
60/40	73
40/60	80
20/80	78
0/100	61

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These results show a benefit for a ethoxylated alcohol to glucoside ratio of 4:1 to 1:4.

## 5 Example 4

When the R =  $C_{11}$  material was mixed in various proportions with SYNPROL SULPHATE (PAS) (a primary alcohol sulphate having a partially branched alkyl chain length of  $C_{13/15}$ , obtained from ICI), the results were:

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PAS/glucoside	% Detergency
ratio (wt)	
100/0	32
80/20	31
60/40	35
40/60	39
20/80	48
0/100	43

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These results show that this PAS does not improve the performance of the glucoside alone, except at a ratio of about 1:4.

# Exampl 5

When R = C<sub>12</sub> alkonyl glucoside was mixed in various proportions with LIAL 125 PAS (primary alcohol

sulphate made from a C<sub>12/15</sub> OXO alcohol with 59% branching and of the branched material 45% butyl or greater), the results were

LIAL 125 PAS/C <sub>12</sub> alkonyl glucoside	% Deterg ncy
100/0	23.96
80/20	28.25
60/40	36.44
40/60	44.28
20/80	49.38
0/110	42.73

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These results show that LIAL 125 PAS improves the performance of C<sub>12</sub> alkanoyl glucoside especially at a ratio of about 1:4.

# 20 Example 6

When R =  $C_{12}$  alkanoyl glucoside was mixed in various proportions with APG 300 (an alkyl poly glycoside with a  $C_{9/11}$  alkyl chain and a degree of polymerisation of 1.4 supplied by Horizon), the results were

% Detergency

53.25

60.14

59.50

56.43

52.98

42.73

APG 300/C<sub>12</sub>

100/0

80/20

60/40

40/60

20/80

0/100

alkanoyl glucoside

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30

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# Example 7

When  $R = C_{12}$  alkanoyl glucoside was mixed in various proportions with pure sodium laurate soap the results were

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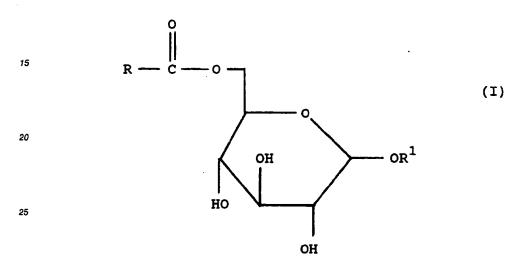
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C <sub>12</sub> Soap/C <sub>12</sub> alkanoyl glucoside	% Detergency
100/0	1.57
80/20	24.66
60/40	42.02
40/60	49.32
20/80	47.18
0/100	38.24

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## Claims

- 1. A fabric washing composition comprising a surfactant system comprising an O-alkanoyl derivative of a reducing hexose sugar and a co-surfactant selected from the group of anionic detergent actives, nonionic d tergent actives, zwitterionic deterg nt actives, amphot ric detergent active s, cationic detergent actives and semi-polar detergent actives except where the anionic detergent active is linear alkyl benzene sulphonate.
- 2. A composition according to claim 1 wherein the O-alkanoyl derivative is 6-0-alkanoyl glucoside.
- 3. A composition according to claim 1 wherein the derivative is an O-alkanoyl glucoside having the formula 10 (I)



- wherein R is an alkyl or alkenyl group hazing from 7 to 18 carbon atoms and R<sup>1</sup> is hydrogen or an alkyl group having from 1 to 4 carbon atoms.
  - 4. A composition according to claim 3 wherein R1 is an ethyl group.
  - 5. A composition according to any preceding claim wherein the weight ratio of O-alkanoyl derivative to cosurfactant in the surfactant system is from 20 to 1 to 1 to 20.
- 6. A composition according to any preceding claim wherein the weight ratio of O-alkanoyl derivative to co-surfactant in the surfactant system is from 9 to 1 to 1 to 9.
  - 7. A composition according to any preceding claim wherein the co-surfactant is selected from primary alcohol sulphates, soaps, ethoxylated alcohols and alkyl polyglucosides.
  - 8. A composition according to any preceding claim wherein the co-surfactant is a primary alcohol sulphate and the weight ratio of O-alkanoyl derivative to PAS is 4 to 1.
  - 9. A method of washing fabrics comprising contacting the fabric with a wash liquor containing a composition according to any one of claims 1 to 8.

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# EUROPEAN SEARCH REPORT

EP 90 31 0763

ategory		th indication, where appropriate,		ievant claim	CLASSIFICATION OF THE APPLICATION (Int. CL5)
X,P	WO-A-8 901 480 (NOVO I * abstract; page 4, lines 20-	•	1-4	,7,9	C 11 D 1/66
X,D,P	EP-A-0 380 437 (NOVO N * page 2, lines 52-55; page		1-3	,7,9	
X,D	WO-A-8 810 147 (NOVO I * abstract; page 3, lines 15- example 9 *	NDUSTRI A/S) 32; page 4, lines 27-29; page	1,2 e 12;		
Α	WO-A-8 000 452 (QUIMIC * abstract *	A MILEN S/A)	1		
Α	GB-A-1 598 102 (TATE & * claims *	LYLE LTD)	1		·
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					TECHNICAL FIELDS SEARCHED (Int. Cl.5)
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Y: p C A: t	CATEGORY OF CITED DOCU particularly relevant if taken alone particularly relevant if combined wit document of the same catagory technological background non-written disclosure	MENTS E h another D L	the filing da document of document of	ite ited in th	ent, but published on, or after e application ther reasons